

1047.525



# PATENT SPECIFICATION

NO DRAWINGS

1047.525

Inventor: KENNETH GEORGE MASON

Date of filing Complete Specification: Aug. 6, 1963.

Application Date: May 30, 1962.

No. 20743/62.

Complete Specification Published: Nov. 9, 1966.

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Index at acceptance:—C2 C(1F4A2, 1F4C7, 1F4D3, 1F4F5, 1D, 2B18, 2B21); A5 E(1C3B1, 1C3B3, 1C4B2, 1C4B3, 1C4B4, 1C5B, 1C5D, 1C6, 1C7B)

Int. Cl.:—C 07 d 63/02 // A 01 n

## COMPLETE SPECIFICATION

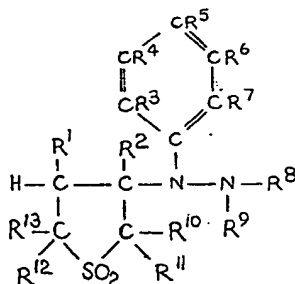
### Sulpholanyl Phenylhydrazines

We, WHIFFEN & SONS LIMITED, a British Company, of Willows Works, Derby Road, Loughborough, Leicestershire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new compounds which possess fungicidal activity.

It has been found that the sulpholanyl phenylhydrazines as hereinafter described are active fungicides with particularly useful activity against certain rusts.

Accordingly the present invention is for the new sulpholanyl phenylhydrazines of the formula:—



or salts or acyl derivatives, wherein in the above formula the groups  $R^1$  and  $R^2$  may be the same or different and may be hydrogen, alkyl (for example of 1—8 carbon atoms such as methyl, ethyl or butyl), substituted alkyl, or alkoxy (for example of 1—8 carbon atoms such as methoxy or ethoxy); the groups  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  may be the same or different and may be hydrogen, halogen (for example chlorine, bromine or iodine), nitro, alkyl (for example of 1—8 carbon atoms such as methyl, ethyl or butyl, substituted alkyl (for example chloromethyl or benzyl),

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alkoxy (for example of 1—8 carbon atoms such as methoxy or ethoxy), amino, alkyl-amino (for example methylamino, ethylamino or octylamino) or dialkylamino (for example dimethylamino or methylbutylamino); the groups  $R^8$  and  $R^9$  may be the same or different and may be hydrogen or alkyl (for example of 1—8 carbon atoms such as methyl, ethyl or butyl), preferably at least one being hydrogen; the groups  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  may be the same or different and may be hydrogen, alkyl (for example of 1—8 carbon atoms such as methyl, ethyl or butyl), substituted alkyl or alkoxy (for example of 1—8 carbon atoms such as methoxy or ethoxy); and the group  $R^{13}$  represents hydrogen or alkyl (for example of 1—8 carbon atoms such as methyl, ethyl or butyl).

According to one embodiment of the invention at least one of the groups  $R^1$  and  $R^2$  is hydrogen, and at least two of the groups  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are hydrogen. According to a further embodiment of the invention the groups  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are hydrogen. According to a preferred embodiment the present invention is for the compound N - phenyl - N - 3 - sulpholanyl - hydrazine, which is of the formula above wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  are all hydrogen.

Salts of the new sulpholanyl phenylhydrazine according to the present invention which may be mentioned include strong acid addition salts such as the hydrochloride or sulphate.

Acyl derivatives which may be mentioned include acyl derivatives of the hydrazine function, such as for example acetyl, propionyl, butyryl or benzoyl derivatives. These may be prepared by reacting the appropriate sulpholanyl phenylhydrazine with an acylating agent.

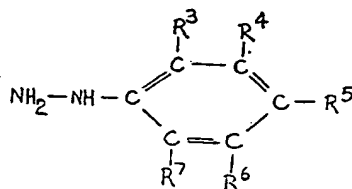
Examples of the new sulpholanyl phenylhydrazines according to the present invention which may be mentioned include:—

- N - phenyl - N - 3 - sulpholanylhiazine  
 N - orthotolyl - N - 3 - sulpholanyl-  
 hydrazine  
 N - metatolyl - N - 3 - sulpholanylhiazine  
 5 N - 2,4 - dinitrophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - 2,5 - dinitrophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - parachlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 10 N - parabromophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - paraiodophenyl - N - 3 - sulphol-  
 anylhiazine  
 15 N - orthochlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - metachlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - 2,4,6 - trichlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 20 N - 2,4,5 - trichlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - 2,3 - dichlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 25 N - 2,4 - dichlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - 3,4 - dichlorophenyl - N - 3 - sulphol-  
 anylhiazine  
 N - phenyl - N - 4 - chloro - 3 - sulphol-  
 anylhiazine  
 30 N - orthotolyl - N - 3 - sulpholanyl - N' -  
 acetohiazide.

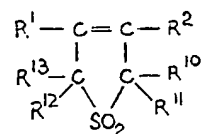
The present invention is also for a fungi-  
 35 cidal composition which contains as an active  
 ingredient a sulpholanyl phenylhydrazine or  
 a salt or acyl derivatives thereof, as identified  
 above. The fungicidal composition may also  
 contain one or more of the materials selected  
 from the group comprising surface active  
 40 agents and solid diluents. The fungicidal  
 composition may comprise a pharmaceutical  
 composition.

The present invention is also for a pro-  
 cess for the treatment of plants, areas of  
 45 ground or materials to prevent fungal growth  
 which comprises treating the plants, areas  
 or materials with a fungicidal composition  
 containing as an active ingredient a sulphol-  
 anyl phenylhydrazine, or a salt or acyl de-  
 50 rivative thereof, as identified above.

According to one embodiment of the pre-  
 sent invention there is provided a process  
 for preparing the sulpholanyl phenylhydrazines  
 as identified above, which comprises warm-  
 55 ing a hydrazine compound of the general  
 formula:



with an unsaturated cyclic sulphone of the  
 formula:



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with or without a small quantity of a strong  
 base, such as for example an alkali metal  
 hydroxide, wherein  $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6,$   
 $\text{R}^7, \text{R}^{10}, \text{R}^{11}, \text{R}^{12}$  and  $\text{R}^{13}$  have the significance  
 indicated above.

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The temperature at which the above pro-  
 cess is carried out depends on the reactants  
 involved. In general, if the time of reaction  
 is to be minimised, temperatures above  $50^\circ\text{C}$   
 but below the decomposition temperature of  
 the sulphone are employed.

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In carrying out the above process an ex-  
 cess of the hydrazine compound is preferably  
 employed. The excess of the hydrazine com-  
 75 pound can be removed on completion of the  
 reaction by distillation or by water washing  
 or by any other suitable means.

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The sulpholanyl phenylhydrazines accord-  
 ing to the present invention are active against  
 a wide range of fungal organisms including  
 80 *Uromyces phaseoli* and *Erysiphe cichor-*  
*racearum*.

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The activity of the various sulpholanyl  
 phenyl hydrazines varies both quantitatively  
 and qualitatively, some compounds possessing  
 a general greater activity than others and some  
 compounds possessing a greater specific  
 activity against certain organisms than the  
 other compounds.

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Certain of the sulpholanyl phenylhydrazines  
 according to the present invention are sub-  
 stantially insoluble in water and may be  
 incorporated in fungicidal compositions in  
 any of the ways commonly adapted for the  
 formulation of insoluble fungicides. Thus for  
 95 example the sulpholanyl phenylhydrazines  
 may be incorporated into an aqueous suspen-  
 sion with or without wetting agents or into  
 an emulsion and/or mixed with solid inert  
 diluents.

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Many salts and other acyl derivatives of  
 the sulpholanyl phenylhydrazines according to  
 the present invention are water-soluble, and  
 a suitable fungicidal composition comprises  
 a solution of the water-soluble sulpholanyl  
 phenylhydrazine or salt or functional de-  
 105 rivative thereof in water.

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Alternatively the fungicidal composition  
 may be formed by dissolving the sulpholanyl  
 phenylhydrazine or salts or acyl derivatives  
 in a water immiscible solvent such as for  
 example a high boiling aromatic hydrocarbon  
 containing dissolved emulsifying agents so as  
 to act as a self-emulsifiable oil on addition  
 to water.

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Similarly the fungicidal composition may be formed by dissolving the sulpholanyl phenylhydrazine or salts or acyl derivatives in an organic solvent, such as for example methyl cellosolve (registered Trade Mark) or ethanol, and the resulting solution used as such or dispersed in water with or without the assistance of a wetting agent. Alternatively the sulpholanyl phenylhydrazine or salts or acyl derivatives may be admixed with a wetting agent or a non-solvent diluent to be used as such or to form a product which is dispersible in water. The sulpholanyl phenylhydrazine or salts or acyl derivatives may also be mixed with a wetting agent, with or without the incorporation of powdered or divided solid materials as referred to above, so that a wettable product is obtained which is capable of use as such or as a suspension or dispersion in water.

The sulpholanyl phenylhydrazine or salts or acyl derivatives may be incorporated for example with solid inert media comprising powdered or divided solid materials, for example clays, sands, talc, mica, fertilizers and the like, such products either comprising dust or larger particle size materials.

The sulpholanyl phenylhydrazine or salts or acyl derivatives may be incorporated for example with solid inert media comprising powdered or divided solid materials, as referred to above, together with a wetting agent, so that a wettable powder is obtained which is capable of use as such or as a suspension or dispersion in water.

The wetting agents used may comprise anionic compounds such as for example soaps, fatty sulphate esters such as dodecyl sodium sulphate, fatty aromatic sulphonates such as alkylbenzene-sulphonates or butyl naphthalene sulphates, more complex fatty sulphonates such as the amide condensation product of oleic acid and the N-methyl taurine or sodium sulphonate of dioctyl succinic acid. The wetting agents may also comprise non-ionic agents such as for example condensation products of fatty acids, fatty alcohols or fatty substituted phenols with ethylene oxide, or fatty esters and ethers of sugar or polyhydric alcohols, or the products obtained from the latter by condensation with ethylene oxide, or the products known as block copolymers of ethylene oxide and propylene oxide. The wetting agents may also comprise cationic agents such as for example cetyl trimethylammonium bromide and the like.

If desired the fungicidal compositions according to the present invention may contain in addition to the sulpholanyl phenylhydrazines or salts or acyl derivatives other agricultural chemicals such as herbicides, fungicides, pesticides, plant growth regulants and the like. According to one embodiment of the invention the sulpholanyl phenylhydrazine or salts or acyl derivatives are mixed with other fungicides such as for

example sulphur, copper compounds such as cuprous oxide or copper oxychloride, nickel compounds such as nickel hydroxide or organic fungicides such as tetramethylthiuram disulphide or salts of ethylene bisdithiocarbamic acid.

The following examples are given to illustrate the present invention. The parts and percentages quoted are by weight unless otherwise indicated.

#### EXAMPLE 1

Butadiene sulphone (59 parts; 0.5 mole) and phenylhydrazine (59 parts; 0.55 mole) were mixed and 0.005 mole (0.6 part) of 40% aqueous caustic potash solution was added. The mixture was kept at 60°C when after 1—2 hours a solid separated. After 10 hours the solid was collected and recrystallized from methanol, giving 105 parts of N - phenyl - N - 3 - sulpholanylhiazine (93% yield) of melting point 119—120°C. The hydrochloride had melting point 189°C. With 2,4 - dinitrobenzaldehyde and para - diamethylaminobenzaldehyde the N - phenyl - N - 3 - sulpholanylhiazine gave hydrazones of melting point 179—182°C and 100—102°C respectively.

#### EXAMPLE 2

The following components were ground together to give a dry powder composition:

N - phenyl - N - 3 - sulpholanylhiazine	20.0 %	
Chain clay (54°D)	55.2 %	
Microsepiolite (powdered Meerscham)	20.0 %	100
Sulphite lye (Wafex—registered Trade Mark)	4.0 %	
Sodium alkylphenolpolyoxyethylene sulphate (Tensiofix WP)	0.8 %	105

#### EXAMPLE 3

A mixture of butadiene sulphone (59 parts), phenylhydrazine (59 parts) and 40% KOH (6 parts; 0.1 equivalent) was kept at 60°C overnight when a solid separated out. Filtration yielded N - phenyl - N - 3 - sulpholanylhiazine (65 parts; 57% yield) of melting point 119—120°C.

#### EXAMPLE 4

Butadiene sulphone (6 parts) and meta-chlorophenylhydrazine base (8 parts) were kept at 60°C for 48 hours. The dark brown material was successively extracted with ether, which removed excess of reactants and left a semi-crystallised solid, which crystallised readily from ethyl acetate—light petroleum mixture, giving N - meta - chlorophenyl - N - 3 - sulpholanylhiazine, of melting point 98—99°C, in a yield of 50%.

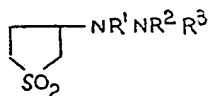
## EXAMPLE 5

A 2% suspension of the formulation of Example 2 in water comprising a suspension containing 400 parts per million of N - phenyl N - 3 - sulpholanylhiazine was painted on the proximal half of the first true leaves of seedling Pinto beans and after drying the whole plants were dusted with spores of *Uromyces phaseoli* and the plants treated as above. Not only did the fungi fail to develop on the treated areas of the leaves, but there was also a complete suppression of its development on the untreated distal half of the leaves.

## EXAMPLE 6

In another experiment cotton wool was wrapped round the petioles of the leaves and soaked in a 2% suspension of the formulation of Example 2. Two days later the plants were dusted with spores and treated as above and there was substantial control of the fungus on the leaves as compared with the development on untreated control plants.

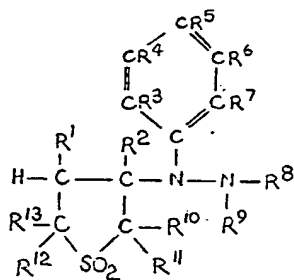
In our patent specification No. 979131 there is described compounds of the formula



and their salts and hydrazides wherein R¹, R² and R³ are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl or sulpholanyl and wherein the sulfolane ring may be further substituted by, for example, alkyl, aryl, hydroxy or hydrazino.

## WHAT WE CLAIM IS:—

1. Sulpholanyl phenylhydrazines of the formula:—



or salts or acyl derivatives thereof, wherein in the above formula the groups R¹ and R² may be the same or different and may be hydrogen, alkyl, substituted alkyl or alkoxy; the groups R³, R⁴, R⁵, R⁶ and R⁷ may be

the same or different and may be hydrogen, halogen, nitro, alkyl, substituted alkyl, alkoxy, amino, alkylamino or dialkylamino; the groups R⁸ and R⁹ may be the same or different and may be hydrogen or alkyl; the groups R¹⁰, R¹¹ and R¹² may be the same or different and may be hydrogen, alkyl, substituted alkyl or alkoxy; and the group R¹³ represents hydrogen or alkyl.

2. Sulpholanyl phenylhydrazines as claimed in claim 1 wherein the alkyl groups contain 1 to 8 carbon atoms.

3. Sulpholanyl phenylhydrazines as claimed in claim 1 wherein the alkyl groups are methyl, ethyl or butyl.

4. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein the halogen is chlorine, bromine or iodine.

5. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein the substituted alkyl is chloromethyl or benzyl.

6. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein the alkoxy is methoxy or ethoxy.

7. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein the alkyl of the alkylamino or dialkylamino is methyl, ethyl, butyl or octyl.

8. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein at least one of R⁸ and R⁹ is hydrogen.

9. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein at least one of the groups R¹ and R² is hydrogen and at least two of the groups R³, R⁴, R⁵, R⁶ and R⁷ are hydrogen.

10. Sulpholanyl phenylhydrazines as claimed in any of the preceding claims wherein the groups R⁸, R⁹, R¹⁰, R¹¹, R¹² and R¹³ are hydrogen.

11. N - phenyl - N - 3 - sulpholanylhiazine.

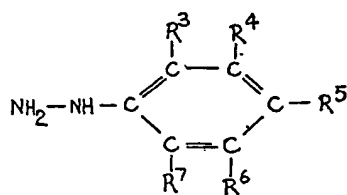
12. N - meta - chlorophenyl - N - 3 - sulpholanylhiazine.

13. Fungicidal compositions which contain as an active ingredient a sulpholanyl phenylhydrazine or salt or acyl derivative thereof as claimed in any of the preceding claims.

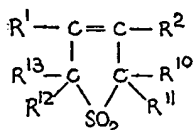
14. Fungicidal compositions which contain a sulpholanyl phenylhydrazine or a salt or acyl derivative thereof as claimed in any of claims 1 to 12 and one or more materials selected from the group comprising surface active agents and solid diluents.

15. A process for the treatment of plants, areas of ground or materials to prevent fungal growth which comprises treating the plants, areas of ground or materials with a fungicidal composition as claimed in claim 13 or claim 14.

16. A process for preparing sulpholanyl phenylhydrazines as claimed in any of claims 1 to 12 which comprises warming the appropriate phenylhydrazine of the general formula



with the appropriate beta-sulpholene of the formula



5 with or without a small quantity of a strong

base wherein  $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^{10}, \text{R}^{11}, \text{R}^{12}$  and  $\text{R}^{13}$  have the significance indicated in claim 1.

17. A process for preparing sulpholanyl phenylhydrazines substantially as hereinbefore described with reference to examples 1, 3 and 4. 10

18. Sulpholanyl phenylhydrazines when prepared by the process as claimed in claim 16 or claim 17. 15

19. Fungicidal compositions substantially as hereinbefore described.

F. MURPHY,  
Agent for the Applicants,  
Chartered Patent Agent,  
Fisons Limited,  
Harvest House,  
Felixstowe, Suffolk.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.